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Synthesis and Structural Characterization of Endohedral Pyrrolidinodimetallofullerene: $La_2@C_{80}(CH_2)_2NTrt$

Michio Yamada,[†] Takatsugu Wakahara,[†] Tsukasa Nakahodo,[†] Takahiro Tsuchiya,[†] Yutaka Maeda,[‡]
Takeshi Akasaka,*[,†] Kenji Yoza,*[,§] Ernst Horn,[¶] Naomi Mizorogi,[#] and Shigeru Nagase*[,#]

Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan, Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-5801, Japan, Bruker AXS, K. K., Yokohama, Kanagawa 221-0022, Japan, Department of Chemistry, Rikkyo University, Tokyo 171-8501, Japan, and Department of Theoretical Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

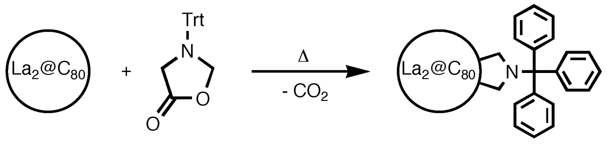
Received September 24, 2005; E-mail: akasaka@tara.tsukuba.ac.jp; yoza@bruker-axs.jp; nagase@ims.ac.jp

Endohedral metallofullerenes present unique structures and properties because the encapsulated metal atom(s) can donate electrons to the fullerene cages.[1] $La_2@C_{80}$ has attracted special attention because of the three-dimensional random motion of two La atoms inside the C_{80} cage.[2−5] To investigate whether the motion of metal atoms encapsulated inside fullerenes is controlled by exohedral addition, density functional calculations were carried out for the $La_2@C_{80}$ derivatives.[6] It is shown that the three-dimensional random motion of two La atoms in $La_2@C_{80}$ can be restricted to the circular motion in a plane by attaching a silicon substituent on the outer surface of the C_{80} cage. Very recently, we have reported the preparation and characterization of the bis-silylated $Ce_2@C_{80}$, in which the motion of two Ce atoms is regulated under a hexagonal ring on the equator by the electron donation from the silyl group to the C_{80} cage.[7] Meanwhile, theoretical calculations[7] predicted that the motion of two La atoms is not regulated in a Diels−Alder cycloadduct, $La_2@C_{80}(C_8H_6(OCH_3)_2)$,[8] in which the addend connects to the C−C bond junction between pentagonal and hexagonal rings (named 5,6-adduct).[6] As may be apparent from the structural and electronic similarities between $La_2@C_{80}$ and $La_2@C_{80}(C_8H_6(OCH_3)_2)$, the attachment of the $C_8H_6(OCH_3)_2$ group has no significant effect on the internal rotation of two La atoms. Such dynamic behaviors of metal atoms encapsulated in various functionalized endohedral fullerenes are of great interest in the field of nanomaterial science.[9]

Since a variety of substituted azomethine ylides can be generated from readily accessible starting materials, various functionalized pyrrolidinofullerenes are obtainable by the Prato reaction.[10−15] We report here for the first time the synthesis and characterization of a pyrrolidinofullerene derivative of $La_2@C_{80}$, $La_2@C_{80}(CH_2)_2NTrt$ (**1**, Trt = triphenylmethyl), and disclose the motion of two La atoms inside the carbon-substituted C_{80} cage.

Two different C−C bonds are available on the C_{80} cage in the reaction with the azomethine ylide. One is the C−C bond between two hexagonal rings (6,6-junction) and another between pentagonal and hexagonal rings (named 5,6-junction). The pyrrolidinofullerene derivative (**1**) was prepared by the thermal reaction of $La_2@C_{80}$ with 3-triphenylmethyl-5-oxazolidinone (**2**)[16] in toluene (Scheme 1). The reaction proceeded smoothly to afford the adduct **1**, which was purified by the preparative HPLC using a Buckyprep column. The matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) mass spectrum of the adduct **1** ($C_{101}H_{19}NLa_2$) exhibits a molecular ion peak at *m*/*z* 1523 and a peak at *m*/*z* 1238 due to a loss of the addend. The visible−near-infrared (vis−near-IR) absorption spectrum of **1** shows an absorption maximum at 668 nm, which differs from the featureless spectrum of the pristine $La_2@C_{80}$ (see Supporting Information). This difference suggests that the π-electronic state of the C_{80} cage is modified by the cycloaddition of the azomethine ylide.

Scheme 1



2 **1**

The ^1H NMR spectrum of **1** exhibits the existence of two isomers (4:1). The major isomer (**1a**) shows two singlet signals at 3.22 and 3.45 ppm, and the minor isomer (**1b**) shows two doublet signals at 2.63 and 4.09 ppm. These ^1H NMR data indicate that **1a** has a plane of symmetry that parallels the pyrrolidine ring, and **1b** has a plane of symmetry that bisects the pyrrolidine ring perpendicularly. The structures of **1a** and **1b** were also investigated by means of ^{13}C NMR spectral analysis. **1a** shows two signals at 44.3 and 62.3 ppm that are assignable to the sp^3-carbon atoms of the pyrrolidine ring, while **1b** shows one signal at 57.8 ppm that is assignable to the sp^3-carbon atoms of the pyrrolidine ring. These suggest that **1a** and **1b** result from the 6,6- and 5,6-additions of the $(CH_2)_2NTrt$ group, respectively.

Isolation of **1a** and **1b** by the HPLC system using various columns was not accomplished because of their similar structures. However, **1a** was successfully purified from the mixture of **1a** and **1b** by recrystallization, and its structure was determined by X-ray crystallographic analysis.[17] Two enantiomeric isomers are observed as a disorder in an asymmetric position of the unit cell.[18] Figure 1 shows the ORTEP drawings of one enantiomeric isomer of **1a**. The ORTEP drawings of another enantiomeric isomer are shown in Figure S13. It is obvious from Figure 1 that **1a** is the 6,6-adduct of $(CH_2)_2NTrt$, as suggested by ^{13}C NMR measurement.

The ^{139}La NMR spectrum of **1a** measured at 278 K shows a broad signal at $\delta = -464$ ppm with a large line-width of 570 Hz, indicative of overlapping of two nonequivalent La atoms. The dynamic behavior of La atoms should be reflected in the ^{139}La NMR line-width. Accordingly, we observed a large broadening of the ^{139}La NMR line-width with increasing temperature from 305 to 363 K for $La_2@C_{80}$ due to the spin−rotation relaxation.[3] In contrast, such a broadening phenomenon of the line-width due to the spin−rotation relaxation was not observed for **1a** upon increasing the temperature from 278 to 313 K, suggesting that two La atoms do not circulate inside the cage, unlike the case of $La_2@C_{80}$.

[†] University of Tsukuba.
[‡] Tokyo Gakugei University.
[§] Bruker AXS.
[¶] Rikkyo University.
[#] Institute for Molecular Science.

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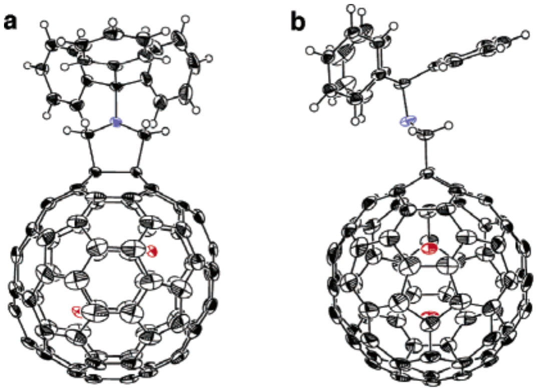

Figure 1. (a) Front and (b) side view of the ORTEP drawings of one enantiomeric isomer of **1a** at 90 K. Thermal ellipsoids are shown at 50% probability level. The hexane molecules are omitted for clarity.

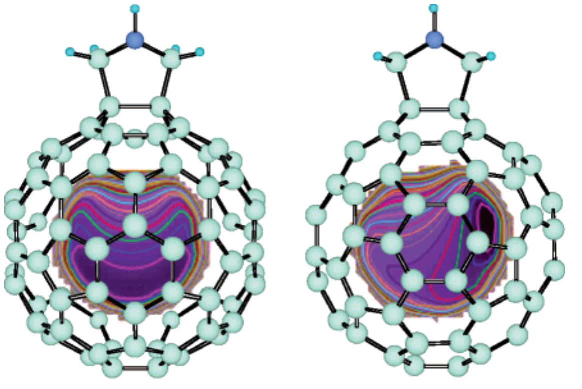
(a) 5,6-adduct **(b) 6,6-adduct**

Figure 2. The electrostatic potential maps of (a) 5,6- and (b) 6,6-$[C_{80}(CH_2)_2NH]^{6-}$.

Theoretical calculations of $La_2@C_{80}(CH_2)_2NH$ show that almost three electrons are transferred from each La to $C_{80}(CH_2)_2NH$, and its electronic structures is formally described as $[La_2]^{6+}[C_{80}(CH_2)_2NH]^{6-}$.[19] The electrostatic potential maps calculated for the 6,6- and 5,6-adducts of $[C_{80}(CH_2)_2NH]^{6-}$ are shown in Figure 2. For the 5,6-adduct, the electrostatic potentials inside the cage are very flat, as calculated for $[C_{80}(C_8H_6(OCH_3)_2)]^{6-}$,[8] and suggest that two La atoms can rotate rather freely. In contrast, the electrostatic potential map for the 6,6-adduct shows a minimum on the mirror plane inside the cage. It should be most highly stabilized when one La^{3+} cation is located near the minimum and the other La^{3+} cation is far away to minimize the electrostatic repulsion between La^{3+} cations. As a result, two La^{3+} cations are fixed, as shown in Figure 1.[20] This was confirmed by optimizing the structure of **1a** using density functional calculations (see Supporting Information).[19] It is noted that the motion of La atoms is controllable by the additional positions.

In conclusion, the 6,6- and 5,6-adducts of a C_{80} endohedral pyrrolidinodimetallofullerenes were successfully synthesized and characterized, and the structure of the 6,6-adduct was fully determined by means of X-ray crystallographic analysis. Two La atoms are fixed in the 6,6-adduct, unlike the random circulation in $La_2@C_{80}$, and can be regulated by additional positions.

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Supporting Information Available: Experimental details and spectroscopic and theoretical data for **1a** and **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Black crystals of **1a**·2(hexane) were obtained by evaporating slowly a solution of **1** in CS_2 and hexane. Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo Kα radiation in the scan range $1.97° < \theta < 27.84°$. Crystal data of **1a**·2(hexane): $C_{110}H_{40}La_2N$, $M_W = 1653.25$, triclinic, space group $P\bar{1}$, $a = 11.0097(11)$ Å, $b = 16.4849(16)$ Å, $c = 18.5435(18)$ Å, $\alpha = 100.1510(10)°$, $\beta = 104.6820(10)°$, $\gamma = 103.9560(10)°$, $V = 3056.9(5)$ Å^3, $Z = 2$, $D_{calc} = 1.796$ Mg/m^3, $\mu = 1.447$ mm^{-1}, $T = 90$ K, crystal size $0.30 \times 0.19 \times 0.06$ mm^3; 47 153 reflections, 13 868 unique reflections; 10 943 with $I > 2\sigma(I)$; $R_1 = 0.0768$ [$I > 2\sigma(I)$], $wR_2 = 0.2216$ (all data), GOF (on F^2) = 1.090. The maximum residual electron density is equal to 1.705 eÅ^{-3}.
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